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## EFFECT OF GRANITE SCREENINGS ON THE PROPERTIES OF ACID-RESISTANT MATERIALS

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The effect of a fluxing additive in the form of granite screenings on the physicochemical properties of acid-resistant materials produced on the basis of high-melting clay was investigated. The effect of the vitreous phase on the sintering process and the main properties of coarse-grained acid-resistant materials is demonstrated.

In manufacture of acid-resistant products refractory clays are now being extensively replaced by high-melting clays that vary in mineralogical, chemical, and granulometric composition.

The studies [1–3] demonstrate the possibility in principle of producing acid-resistant materials based on high-melting clay, quartz porphyrite, and other materials. In spite of different approaches to the problem of producing high-quality acid-resistant materials, the purpose remains the same, namely, formation of a phase composition in ceramic crock that would provide high chemical resistance, mechanical and thermal strength, waterproofness, and other properties.

The main raw materials for acid-resistant articles are sinterable clays of medium and high plasticity that do not contain toxic impurities in the granular state (siderite, lime, gypsum, etc.) in large quantities. In particular, it is indicated in [4] that such clays should contain (here and elsewhere in wt.%): 16–32 Al<sub>2</sub>O<sub>3</sub>, 55–70 SiO<sub>2</sub>, less than 3.5 Fe<sub>2</sub>O<sub>3</sub>, less than 2 CaO.

With the aim of expanding the available natural resources for production of acid-resistant materials, a high-melting clay of the following chemical composition was investigated (%): 59.5–63.2 SiO<sub>2</sub>, 15.2–17.8 Al<sub>2</sub>O<sub>3</sub>, 5.5–6.8 Fe<sub>2</sub>O<sub>3</sub>, 0.6–0.8 TiO<sub>2</sub>, 0.6–2.0 CaO, 1.0–1.48 MgO, 1.2–1.85 K<sub>2</sub>O, 0.2–0.3 Na<sub>2</sub>O, and 8.2–10.3 calcination loss. This clay has a rather wide sintering interval (around 100°C) and sinters within the temperature range of 1050–1100°C. Favorable factors for sintering are high dispersion, a low carbonate content, and a moderate quantity of quartz. A special feature of the chemical composition of this clay is a low content of alkali oxides (R<sub>2</sub>O), which, however, is compensated in sintering by the large amount of finely dispersed Fe<sub>2</sub>O<sub>3</sub>, which acts as a flux, although ferric oxide has a negative effect on the acid resistance [1, 4].

Experimental samples were prepared by plastic molding. Granite screenings were added to the clay and chamotte prepared from the same clay, and the resulting plastic mixture was used to mold tiles of size 50 × 50 × 20 mm, which were fired in the air-dry state at temperatures of 900, 1000, 1050, and 1100°C with a hold at the maximum temperature for 1 h.

Physicomechanical tests to determine the strength, porosity, water absorption, thermal resistance, waterproofness, and acid resistance of fired samples were carried out in accordance with standard methods.

The phase composition was studied by the x-ray method. Diffraction patterns were registered using DRON-3 and URS-50 diffractometers (Cu<sub>α-q</sub> radiation). The diffraction pattern of the initial clay (Fig. 1) exhibits α-quartz, kaolinite, montmorillonite, and illite.

The chemical resistance of fired samples without additives in concentrated H<sub>2</sub>SO<sub>4</sub> corresponds to GOST 474–90. However, the water absorption, waterproofness, heat resistance, and other parameters do not meet the requirements of the standard.

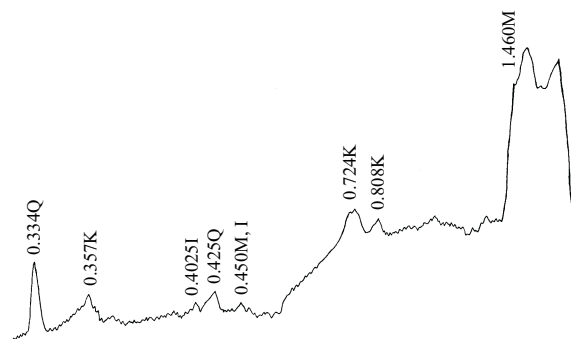


Fig. 1. X-ray phase analysis of Gorodok deposit clay: Q) α-quartz; K) kaolinite; M) montmorillonite; I) illite.

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TABLE 1

Oxide	RO : R <sub>2</sub> O ratio			
	1.40	1.30	1.13	1.11
SiO <sub>2</sub> : Al <sub>2</sub> O <sub>3</sub>	3.78	3.83	3.84	3.84
SiO <sub>2</sub> : R <sub>2</sub> O	17.33	18.74	22.89	28.00
RO : (R <sub>2</sub> O + RO + Fe <sub>2</sub> O <sub>3</sub> )	0.57	0.25	0.24	0.26

It is possible to improve these parameters by more complete sintering. It is known that sintering proceeds with the participation of the liquid phase, which has a significant effect on the structure formation and properties of the material. An increase in the reactivity of the liquid phase with respect to the crystalline components of the mixture makes it possible not only to intensify the sintering process but also to decrease the fuel consumption. A fluxing effect in ceramic mixtures is produced by materials containing R<sub>2</sub>O, RO, and Fe<sub>2</sub>O<sub>3</sub>, which mostly passes over to the vitreous phase.

The resistance of the synthesized material to mineral acids depends on the chemical composition of the vitreous phase and on the perfection of the structure of the crystal phases that form. Thus, quartz and mullite, which have a perfect crystalline structure, are more acid-resistant than crystalline phases containing alkali-earth oxides. The fluxing additives facilitate recrystallization and perfection of the structure of the crystal phases and improvement of their chemical resistance. Taking this into account, the effect of natural materials as fluxing additives, in particular, granite screenings, on the properties of acid-resistant materials was investigated.

The choice of this additive was due to the fact that it contains a substantial amount of R<sub>2</sub>O and RO and belongs to feldspar materials.

Granite screenings are a by-product fraction of sieve concentration of granite. Its chemical composition is as follows (%): 63–65 SiO<sub>2</sub>, 14–16 Al<sub>2</sub>O<sub>3</sub>, 5–7 R<sub>2</sub>O, 4–6 Fe<sub>2</sub>O<sub>3</sub>, and 3–5 RO. The phase composition is represented by anorthite CaO · Al<sub>2</sub>O<sub>3</sub> · 2SiO<sub>2</sub> and α-quartz.

It is known [1] that the physical and technical properties of fired samples depend on the ratio of the oxides in the mixture. Various quantities of granite screenings were introduced into the experimental-mixture composition, as a result of which the RO : R<sub>2</sub>O ratio varied from 1.4 to 1.0. Likewise, the ratio of other oxides that had an effect on the vitreous-phase formation, density, and strength of the samples varied (Table 1).

The dependence of the main properties of the samples on the RO : R<sub>2</sub>O ratio is shown in Fig. 2.

As the RO : R<sub>2</sub>O ratio decreases, the investigated mixture exhibits minimum water absorption and high mechanical strength and density after firing. An increase in the SiO<sub>2</sub> : R<sub>2</sub>O ratio (to 28) results in an increased amount of the vitreous phase and partial dissolution of SiO<sub>2</sub>, which is corroborated by the minimum water absorption. A positive effect on the properties of the acid-resistant materials is produced by the iron-bearing melt, which can be characterized

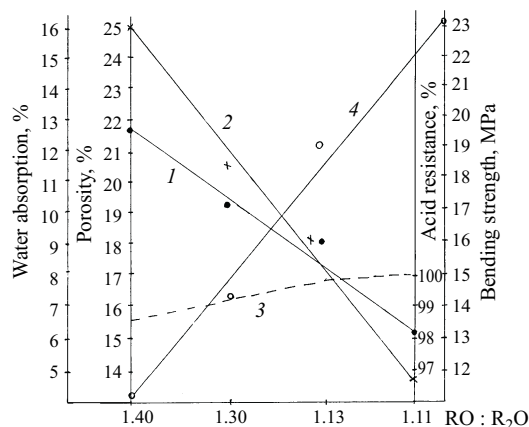


Fig. 2. Dependence of sample properties on the RO : R<sub>2</sub>O ratio: 1) water absorption; 2) porosity; 3) acid resistance; 4) bending strength.

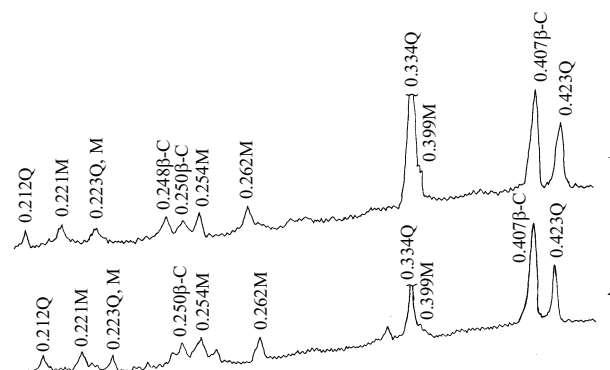


Fig. 3. X-ray pattern of a mixture with an RO : R<sub>2</sub>O ratio equal to 1.13 before (1) and after (2) sulfuric acid treatment: Q) α-quartz; M) mullite; β-C) β-cristobalite.

by the ratio RO : (R<sub>2</sub>O + RO + Fe<sub>2</sub>O<sub>3</sub>), which is equal to 0.24–0.26 in this case. With this ratio, the acid resistance reaches 99%. At 1050°C, a reactive liquid phase is formed that intensifies the dissolution of alumina and silica, which increases the thermal resistance of the samples. After testing in concentrated H<sub>2</sub>SO<sub>4</sub>, the reflections of quartz, mullite, and cristobalite virtually do not change (Fig. 3).

Thus, oxide ratios that affect the sintering, strength, density, thermal resistance, and acid resistance of the ceramic mixtures are identified. In using high-melting clays, optimum properties of the acid-resistant materials are achieved with the ratio RO : R<sub>2</sub>O equal to 1.11–1.13, RO : (R<sub>2</sub>O + RO + Fe<sub>2</sub>O<sub>3</sub>) equal to 0.25–0.35, and SiO<sub>2</sub> : R<sub>2</sub>O equal to 18–22.

The sample of optimum composition has the following properties: water absorption 6.2%, porosity 13.6%, bending strength 22.5 MPa, thermal resistance 14 thermal cycles, acid resistance 99%, and TCLE  $6.7 \times 10^{-6} \text{ K}^{-1}$ .

Based on the data obtained, the conclusion is made that high-melting kaolinite-hydromica clay with a montmorillo-

nite admixture can be used in production of coarse-grained acid-resistant articles.

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